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Formulation of Toughened Paste Adhesives for Reduced-Pollutant Electron Beam Repair and Assembly of Composite Structures

by James M. Sands, Steven H. McKnight, and Bruce K. Fink

ARL-TR-2270

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Army Research Laboratory

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Weapons and Materials Research Directorate, ARL

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Abstract

Historically, e-beam processed resins resulted in brittle matrix materials that were ineffective in meeting the performance demands of the military, largely because the resins lacked toughness. Toughness is a critical parameter of resins that determines the ability of the resin to absorb energy and resist crack growth under stress. The U.S. Army Research Laboratory (ARL) has developed the first high-performance adhesive paste cured by e-beam for bonding and repair of military PMC structures. This new material, ADEP01, is a low-pollutant technology with the potential to replace mechanical fasteners and autoclave processed adhesives for repair and assembly in military applications. ADEP01 was developed from interpenetrating polymer network (IPN) architecture as a two-part paste adhesive. The chemistry of ADEP01 is presented as well as selected design parameters that influenced the development of this class of adhesive pastes. The method of processing and the development of in situ toughening during processing are presented. Further, the performance of ADEP01 is compared to traditional aerospace-grade adhesives, demonstrating the feasibility of designing high-performance e-beam cured materials.

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1. Introduction

Future demands for lightweight, rapid-strike ground and air vehicles, as described in current projections for Army After Next (AAN) combat forces, will require an increased use of composite structures in Army systems [1]. The composite solutions that are envisioned, particularly polymer matrix composites (PMCs), are actually multimaterial multifunctional assemblies that are adhesively bonded. There is a need to effectively join the layers in these structures since the individual constituents are structural subelements. The methods of assembly and repair must be cost effective, amenable to thick sections, and meet the necessary performance criteria, often including the return of ballistic, fire-protective, structural, and electrical properties. Furthermore, one can project a need for efficient and effective repair methods that will require high-performance adhesives.

Looking forward, multifunctional composite structures present challenges to the effective fielding of PMCs in ground vehicle applications. PMC manufacturing and repair processes result not only in a repaired or manufactured part but also in hazardous waste, hazardous emissions, and solid waste. A recent study assessed the type and quantity of pollutants from a number of composite manufacture and repair process techniques [2]. Using current production methods, the expanded use of composite materials will lead to an increased waste stream (trim, consumables, volatile organic compound [VOC] emissions) from assembly and repair, an increased hazardous waste stream due to shelf life expiration (refrigeration), and an increased dependence on autoclave processing (NO_x). Eliminating or minimizing the contribution of composite repair and remanufacture to the waste stream will grow in importance as the use of composite materials expands. Consequently, the Department of Defense (DOD) requires (1) a reassessment of current repair procedures; (2) the maturation of new technologies that reduce hazardous emissions and waste due to repair; and (3) the redesign and remanufacture of components incorporating new technologies that maximize the opportunity for practical, affordable, and reliable repairs. Any new technologies are expected to reduce environmental impact and its associated costs.

Although no single solution can reduce the environmental impact of the entire range of materials, applications, and processing scenarios for composite repair and remanufacture throughout DOD, there are a number of approaches to mitigate environmental impact. Reducing the production of hazardous emissions and wastes can be achieved by a reduction in shelf-life limitations, incorporation of localized heating, reduction in processing steps, and containment and recycling of VOCs. In general, new materials that can be cured out-of-autoclave will be key to meeting hazardous waste reduction efforts.

Rapid joining capabilities for PMC manufacture include nonautoclave techniques for curing thermoset adhesives such as induction [3], ultraviolet (UV) [4], and electron beam (e-beam) [5] processing. E-beam and UV curing methods have been extensively evaluated in coatings applications and show considerable promise as alternative curing strategies for thermoset PMCs [6], while induction curing has the greatest potential for implementation into a portable repair unit [7]. Each of these alternative methods of manufacture will eliminate or minimize the use of autoclave curing and may produce resins with extended shelf life. Technical barriers that need to be addressed for the environmentally friendly alternative cure and processing methods to gain acceptance include formulating toughened resins and adhesives, optimizing process parameters, and demonstrating acceptable performance. The work presented here seeks to develop extended shelf life resins with equivalent or improved performance to currently existing products for various military applications.

When considering thermoset adhesives for repair of composite materials, shelf life becomes a major environmental and economic consideration. Most adhesive and composite material resin systems cure slowly during storage. For these systems, processing and performance requirements can be met only within the designated storage period or shelf life (Figure 1). Shelf-life limitations for commonly used composite material systems and adhesives are shown in Tables 1 and 2, respectively. No commercially available structural adhesives approved for use in DOD applications having a shelf life longer than 12 months have been identified. Shelf life is generally listed for a required level of reduced-temperature storage. Once the partially cured material is removed from cold storage, the limit on useful life is called “out-time.”

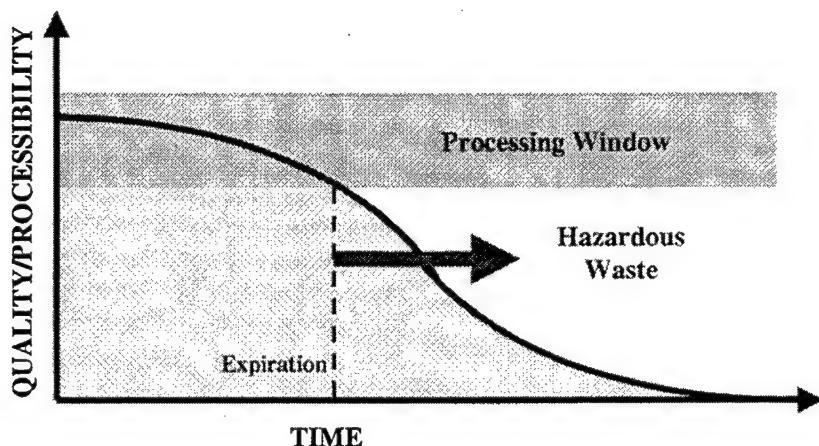


Figure 1. Shelf Life Expires When Material Processing Characteristics No Longer Meet Specification Limits.

Table 1. Shelf-Life Limitations of Commonly Used Composite Materials [8]

Resin/Fiber System	Processing Temperature (°F)	Service Temperature (°F, Dry)	Shelf Life at 0 °F (Months)	Out-Time at RT ^a (Days)
Epoxy/Carbon Fiber	250–350	180–450	6–12	10–30
Epoxy/Aramid Fiber	250–285	250	6	10–30
Epoxy/S-2 Glass Fiber	250–350	250–350	6	12
Bismaleimide/Carbon Fiber	350–475	450–600	6	28
Cyanate Ester/Carbon Fiber	250–450	450–480	12	30
Cyanate Ester/Quartz Fiber	250–350	200–350	6	21
Polyimide/Quartz Fiber	550–650	600	6	10

^aRoom temperature.

Materials that have exceeded shelf life or out-time are partially cured beyond acceptable limits, can no longer be used, and are considered hazardous waste under Resource Conservation and Recovery Act (RCRA) specifications [9]. Epoxy and other commonly used resins have finite shelf lives and must be disposed of after expiration, creating unnecessary and expensive (\$25–50/lb) waste. A 1995 report contends that each year millions of pounds of expired material and associated packaging are processed for disposal by DOD [10].

Table 2. Shelf-Life Limitations of Commonly Used Adhesives

Adhesive System	Processing Temperature (°F)	Service Temperature (°F, Dry)	Shelf Life at <40 °F (Months)	Shelf Life at <77 °F (Months)	Out-Time at RT ^a
Hysol EA 9390 Two-Part Epoxy Paste [11]	200	350	12	6	2 hr
Hysol EA 9394 Two-Part Epoxy Paste [12]	RT	350	12	12	1.5 hr
Hysol EA 9396/C-2 Two-Part Epoxy Paste [13]	200	400	12	12	8 hr
Hysol EA 9695 Epoxy Film [14]	250–350	300	6 at 0 °F	3	90 days

^a Two-part paste out-times are after mixing.

Hazardous waste generated as a result of shelf life expiration can be eliminated by using alternative processing where appropriate. Furthermore, the number of processing steps can be reduced by combining processing steps through co-injection and, to a lesser extent, with localized heating. Co-injection involves the simultaneous processing of different resins into a single component. VOC emissions are reduced primarily by rapid curing, which ensures that low-molecular-weight materials polymerize before evaporating, thus providing large reductions in the production of volatile species. Shelf life expiration can also be eliminated by remanufacturing thermoset-based composite components with thermoplastic-based designs and processes. The work reported here addresses the shelf life issue because the development of an extended shelf life for resins, and in particular adhesives for repair, will greatly reduce the environmental impact of increasing composite usage.

Addressing issues related to environmental pollution control requires the introduction of new materials technologies that have a reduced environmental impact while providing equivalent or improved materials performance. E-beam curing technology has been earmarked as an enabling technology for fabricating affordable integrated composite assemblies and has been rapidly maturing over the last 5 yr. E-beam curing of composite materials is achieved by using a stream

of high-energy electrons to activate cross-linking in polymers that are modified to be radiation sensitive. E-beam curing is a nonthermal process that eliminates the temperature, pressure, and size demands of the traditional autoclave cure. Consequently, the development of e-beam curable resins and adhesives is a crucial facet to both environmental and economic advancement in materials design.

The greatest limiting factor in the widespread acceptance of alternative cure technologies has been deficient performance of alternative-cure adhesives and resins. This report discusses progress in alternative-cure adhesive technology for reduced environmental impact and improved performance. A new class of e-beam-cured adhesives is presented, which demonstrates that alternative-cure techniques can effectively replace thermal and autoclave repair methods in both present and future applications. We demonstrate that these new materials are designed to exceed the performance of current adhesive repair methods. The state of the art in alternative-cure technology, particularly e-beam, has not previously achieved the performance criteria, such as adhesive toughness, of traditional thermal and autoclave-cured adhesives. We demonstrate that both toughness and durability can be achieved in alternative-cure adhesives by designing innovative materials. Furthermore, the e-beam-curable adhesive formulations have dramatically improved shelf-life stability compared to current products. From the results demonstrated in this report, reducing environmental impact while increasing the applicability of composites can be achieved through materials design and incorporation of new technological approaches.

2. Background

Alternative curing of composites and adhesives has great potential for lowering the cost and environmental impact of manufacture and repair of military composite structures. In 1989, the Department of Energy (DOE) recognized the importance of developing new technologies for the manufacture of composite resin systems [15]. The potential advantages from e-beam curing techniques include six key process improvements:

- (1) *Improved resin stability.* Radiation-cured resins are much more stable at room temperature. Thus, a longer shelf life of the monomer materials can be realized for e-beam materials and reduce hazardous waste disposal.
- (2) *Increased complexity of materials manufactured.* By decreasing the processing temperatures associated with cure of the composite, more complex parts can be realized. The advantage of decreased part shrinkage and warpage will couple with low-cost tooling to improve shape variability in composite manufacture.
- (3) *Control of the extent of curing and improved uniformity of material cure.* Because e-beam curing is a radiative process, the input parameters for a given shape can be varied as necessary to ensure complete curing of the composite.
- (4) *Reduction in curing time.* Curing of composite materials can be accomplished in a few minutes, rather than the multiple hours necessary to complete a thermal cure under autoclave conditions.
- (5) *Reduction in volatile emissions.* Elimination of volatile organic compounds, which result from the cure mechanisms associated with thermally cured resins, as well as the reduced use of autoclaves for curing, will diminish the volatile emissions associated with composite manufacture.
- (6) *Reduction in tooling costs.* E-beam curing is a room-temperature curing process. Therefore, the need for expensive metal tooling can be replaced by low-cost wooden or plastic/foam molds.

Studies performed by Janke et al. under DOE funding resulted in improvements in resin quality for e-beam applications [15]. However, the implementation of the materials produced under this DOE funding resulted in composites far too brittle for most composite applications. Attempts at toughening these resins resulted in detrimental effects on the critical resin properties including

modulus and glass transition. Further, the adhesives formulated under this program lacked toughness and bond strength, which has hindered use of e-beam curing by manufacturing companies.

There are two common cure chemistries for inducing cure by irradiation: (1) vinyl-based systems, which cure via a free radical chain addition mechanism, and (2) epoxy-based systems, which cure through step growth chain polymerization. Examples of free radical curing resins are unsaturated polyester, urethane acrylates, epoxy acrylates, and methacrylates, which have double bonds capable of sustaining free radical chain polymerization initiated by radiation. These systems are by far the most widely used radiation curable materials. Their use is commonplace in furniture, medical, and electronics industries. Examples of cationic and free radical curing initiation and propagation are demonstrated in Figure 2, where cationic cure occurs through the ring-opening of epoxides and free radical cure involves polymerization through unsaturated bonds. A cationic catalyst [e.g., diphenyliodium hexaflouroantimonate ($(C_6H_5)_2I^+ \cdot SbF_6^-$)] is used to initiate the homopolymerization of the epoxides under e-beam irradiation. Upon irradiation, the catalyst produces a Bronsted acid ($H^+SbF_6^-/HF$) which promotes the ring-opening of the epoxide and a stabilized cation. Although the primary reaction pathway to forming polymer involves propagation through the epoxide ring-opening, many other mechanisms of reaction are present during the curing stage, including chain propagation, chain transfer, and termination. The complex mechanisms for cationic radiation cure of epoxides have been studied rarely, but Pascault has reported on some mechanisms [16]. Free radical initiation occurs through excitation of the π -electrons in the alkene to generate radicals and therefore does not require a catalyst under e-beam cure. The free radical system can be cured using thermal and UV excitation methods by selecting an appropriate catalyst.

The development of e-beam adhesives has been addressed from three approaches: (1) cationic epoxy network systems; (2) free radical vinyl ester and methacrylate systems; and (3) interpenetrating polymer networks (IPNs). Each of these approaches has advantages. For example, cationic e-beam-cured epoxy systems have higher glass transition temperatures (T_g) than the traditional free radical systems. Some of the cationic cure systems have T_g 's that rival

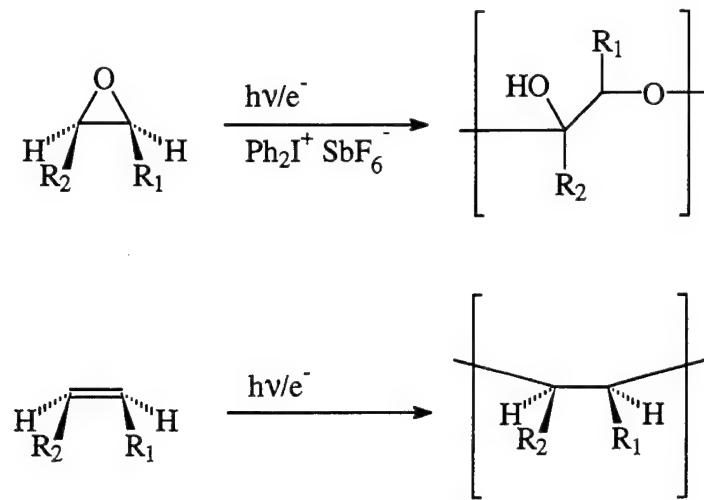


Figure 2. Examples of Simple Reactions for Formation of Polymers From Cationic E-Beam Cure of Epoxides and Free Radical E-Beam Cure of Alkenes.

those of the best polyimides (i.e., >350 °C), but these materials lack mechanical integrity [17]. Free radical-cured materials are prepared using a monomer that has a very long shelf life. The raw materials for free radical networks are unsaturated hydrocarbons, which have excellent stability in the presence of inhibitors and the absence of oxygen [18], which may lead to improved shelf life.

One of the key advantages to IPN adhesives, however, is the ability to B-stage and C-stage the adhesive through a thermal cure, imparting varying levels of mechanical integrity before e-beam curing is applied. The B-stage (represented in Figure 3) of an IPN is the state where the thermal-cured epoxy is controlled to prevent a high degree of cross-linking. B-stage resin can be acquired by partial curing of the epoxy network or through end-capping of a fully cured epoxy network, thus increasing the number of chain ends and decreasing the molecular weight of the epoxy network. In the other extreme, a C-stage epoxy network is formed by driving the epoxide reaction beyond the critical conversion for gelation. Two-part paste adhesives are formulated so that after thermal curing the resin is C-staged (i.e., cured beyond the critical conversion); the resin will no longer flow due to temperature changes. Further, the C-stage has reached maximum shrinkage for thermal curing. E-beam is applied to the C-stage network to achieve a complete IPN cure. A key property in the C-stage of two-part paste adhesives is the strength of the bond formed after only thermal cure, or green strength. Because the IPN is partially formed

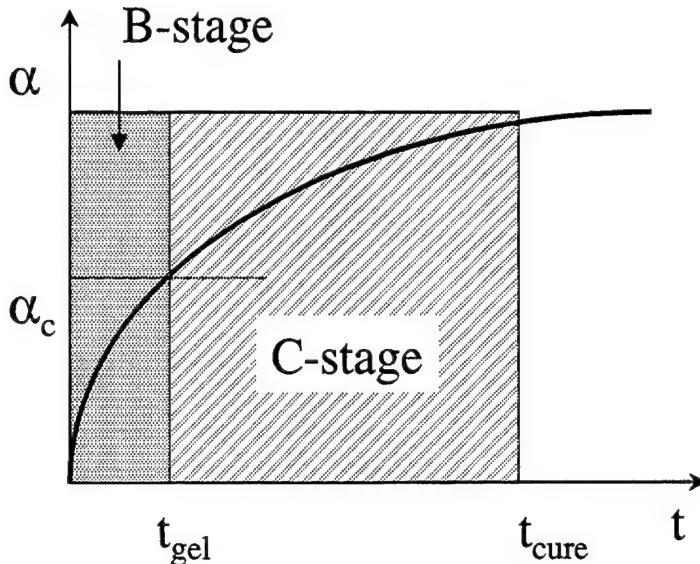


Figure 3. Representative Plot for Cure Conversion (α) vs. Cure Time (t). The Definitions of B-Stage and C-Stage Are Defined Relative to the Gelation Time (Also the Critical Conversion, α_c) and the Time for Complete Cure. Cure Completion Beyond the Critical Conversion Is Presumed to Produce a C-Stage Network Structure in the Sequential (Seq) IPNs.

under thermal cure, materials bonded with a significant green strength are easy to transport for remote e-beam curing. In some instances, such as developing one-part pastes and films, B-stage network formation of the epoxy may be preferable. By varying the functionality of the epoxides and amines utilized in the formulations, a range of B-stage and C-stage materials can be generated for different applications.

The IPN approach for e-beam resin development combines advantageous properties from both cationic and free radical systems. Namely, the high-temperature stability of cationic systems and the monomer stability of free radical systems are achieved through IPN chemistry. The high-temperature stability of e-beam-cured IPNs is achieved through a two-stage curing process, which incorporates a thermal cure (50–80 °C) of an epoxy-amine network, followed by e-beam curing of a free radical network [20]. The stability of free radical systems is imparted to the resins through monomer blending. Among the unique advantages of using an IPN system are the ability to C-stage, or partially cure the composite (e.g., thermally cure the epoxy), as shown schematically in Figure 4. Depending upon the IPN composition, C-stage composites range

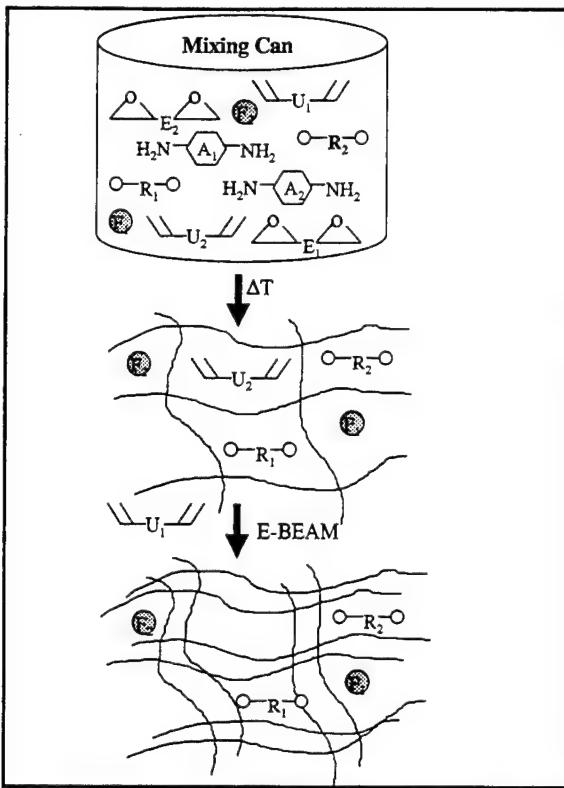


Figure 4. Cure Scheme for IPN Formation. Representative Materials Include Amines (A_1 , A_2), Epoxides (E_1 , E_2), Unsaturated Hydrocarbons (U_1 , U_2 , R_1 , R_2), and Unreactive Fillers (F_1 , F_2).

from a rigid network to a sticky gum. The C-stage composite is a fully cured epoxy-amine with epoxide conversion approaching 100%. Subsequent e-beam curing at a defined radiation dose results in high conversion of the unsaturated sites via free radical propagation and produces the fully cured composite [21]. This multiple-stage curing approach provides a mechanism for eliminating the transport of the fabrication mold to the e-beam facility. A significant advantage for IPNs over cationic chemistry systems is the lack of complications from impurities, especially nitrogen and nitrogen-containing species, which are notorious for polluting the cationic e-beam catalyst [22]. Compared to traditional free radical cured e-beam materials, the IPNs provide the additional advantage of reduced shrinkage on cure. Typical free radical cured systems shrink an average of 4–20% on curing due to the conversion of van der Waals intramolecular interactions into covalent bonds [18]. In IPN structures, the degree of shrinkage ranges from 2 to 8%, half of which occurs during the thermal curing of the epoxy network [23].

Although the residual stress buildup during the formation of the IPN network has not been characterized in this effort, a few comments can be made regarding the expected impact of cure shrinkage on mechanical properties. During the C-stage formation, the resin shrinks due to the formation of covalent bonds. The degree of shrinkage varies during the thermal cure with the representative concentration of epoxides and amines in the adhesive; however, once the system reaches full cure, the T_g of the C-stage material can be measured. The T_g is shown to be ambient to sub-ambient (broad T_g between 18 and 32 °C). Consequently, residual stresses that are generated due to thermal curing should relax from the network before e-beam curing occurs. Following e-beam curing, the epoxy network acts as a rigid template to minimize further shrinking of the system. The residual stresses that develop during e-beam curing have not been measured. However, some experimental evaluations have shown that post-e-beam heating of the samples can improve reproducibility of lap-shear measurements, which may result from relaxation of stresses developed during the e-beam step.

The results from "toughened" e-beam-curable adhesive formulations are compared to thermally cured epoxy adhesives. We evaluate adhesive materials in three categories: two-part paste adhesives, one-part paste adhesives, and film adhesives. The greatest success has resulted from our development of a two-part paste adhesive for e-beam cure, and therefore the data presented in this report are for two-part paste adhesives.

The benchmarks for successful development of an e-beam curable adhesive are commercially available thermal-cured epoxy pastes, cationic e-beam adhesives developed under the 1992 DOE program, and commercial free radical e-beam adhesives. The best aluminum (Al)-aluminum shear results available are listed for some commercial materials in Table 3. The best commercial systems demonstrate lap shear strength (LSS) >6000 psi on treated aluminum substrates.

Another method of screening adhesive performance is to evaluate the adhesive resin for fracture toughness (G_{IC}). A resin demonstrating both a high fracture toughness (>3 kJ/m²) and a high Al-Al LSS (>4000 psi) is a candidate for most high-performance applications. Table 4 lists a number of classes of resin systems, which are available in research or commercial markets,

Table 3. Benchmark Thermal Standards for E-Beam Adhesive Development With Baseline Values Provided for Common Repair Paste Adhesives

Trade Name	Manufacturer	Al-Al LSS (psi)	T _g (°C)	References
NG1 (Cationic)	Northrup Grumman	—	350	—
EA9628 (Film)	Dexter Hysol	5700	180	—
EB17D	ORNL ^b	2600	N.R. ^d	—
AP-299	SRL, ^c Inc.	3700 ^a	100	Goodman and Byrne [24]
AP-408	SRL, Inc.	3200 ^a	100	Goodman and Byrne [24]
EA9394	Dexter Hysol	3600	78	—
FM73M (Film)	CYTEC Engineered Materials, Inc.	6300	95	CYTEC Engineered Materials, Inc. [25]
H4800 (Methacrylate)	Dexter Hysol	4500	N.R. ^d	—

^a Results from composites affordability initiative (CAI) program, January 1999.

^b Oak Ridge National Laboratory.

^c Scientific Research Laboratory.

^d Not reported.

Table 4. Range Variability in Fracture Energy for Selected Resin Systems

Material Type	G _{IC} (kJ/m ²)	LSS (psi)
Cationic E-Beam	0.2–0.45	250–1500
Thermal Epoxy (Paste)	3.0–5.9	3500–4200
IPN E-Beam	1.1–2.4	3000–6000
Toughened Films	2.5–3.5	4500–6500

along with the fracture toughness and LSS ranges for these generic classes. The best performing adhesives are toughened epoxy films such as CYTEC Engineered Materials, Inc.'s FM73 adhesive. However, these materials often are less user friendly (i.e., possess short out-time or shelf life) and invite a high cost to most applications.

3. Fracture Toughness Mechanisms

Among the merits of elastomer-epoxy and thermoplastic-epoxy multiphase dispersions is the large gain in toughness accomplished with minimal loss in the tensile strength, modulus, and

thermal mechanical properties over neat epoxy. Common to all toughened thermoset networks that exhibit high modulus and strength is a highly cross-linked base matrix resin filled with a noncompatible thermoplastic or rubber. The incompatibility of the second phase blended with the monomer resin simplifies processing issues. Upon curing the thermoset, the toughening agent becomes incompatible and separates into dispersed particles. The most evaluated thermoplastic materials for toughening of brittle epoxy networks are poly(ether sulfone) and polysulfone [26]. These polymers have aromatic structures that make them highly soluble in the bis-phenol-based epoxy monomers. The most commonly used materials for toughening in low-temperature thermosets are synthetic rubber co-polymers called carboxyl terminated butadiene nitriles (CTBNs) which are chemically designed to phase-separate during epoxy network formation [27].

Preparation of toughened thermosets using CTBNs, thermoplastics, and dendrimers is accomplished through either a thermodynamic/kinetic or a mechanical approach. The thermo/kinetic approach involves using a dissolved rubber in the resin and relying on phase separation to produce randomly distributed particles or co-continuous toroidal morphology. The mechanical approach involves prefabrication of particles and blending and dispersing the particles into the resin at selected volume fractions. Either method may be preferred under specific preparative constraints. One should be aware that improving toughness is often accompanied by a reduction in other target material properties. An optimum balance between matrix toughness and other key properties such as glass transition temperature must be accomplished through empirical studies or through molecular modeling [28]. Although the ideal approach is to apply a molecular-level model, an empirical approach is necessary to verify the model results and determine a set of parameters to explore more closely with a model.

Understanding the key mechanisms of toughening thermoset resins is important to the design approach taken in toughening. Reported mechanisms of toughening generally address two issues: (1) the mechanics of the failure, associated with microstructure changes in the system, and (2) the energetics of failure, which propose that the macrostructure and interfacial interactions are key to energy dissipation during loading. Some research groups hold that

toughening is achieved through the modification of the microstructural features in the resin material, while others believe that the interfacial interaction between the matrix and the toughening agent is the key. Unfortunately, these two concepts are not easily separated using experimental methods. However, the general knowledge of the failure modes in thermoset materials is extensive. A brief list of failure mechanisms is presented in Table 5, along with a description of the mode and a list of key parameters to inducing/observing this form of failure. Understanding these mechanisms and their relation to the structure of the polymer is essential to properly designing toughened systems.

Table 5. Mechanisms of Failure in Thermoset Materials

Mechanism	Definition	Key Parameters	Author Citations
Crack Pinning	Crack front changes in length as it interacts with heterogeneous particles.	-Particle diameter (d_p). -Particle separation (d_s).	Lange [30] Evans [31] Rose [32]
Particle Bridging	Particle acts as a bridge across the wake of the forming crack, applying a compressive traction. The ductile particles plastically deform.	-Favors large particles (d_p).	Sigl et al. [33]
Crack-Path Deflection	Decrease the mode-I fracture and increase the mode-II (shearing) character of the material.	-Particle size is an independent variable. -Particle separation and distribution are key (d_s).	Faber and Evans [34]
Shear Banding or Shear Yielding	Massive shear banding occurs at the stress tip (specifically for rubber toughened materials).	-Uniformly spaced particles (d_s). -Favors small particles (d_p). -Particles are initiation sites for matrix yielding.	Argon [35] Kim and Brown [36] Pearson [37] Wu [38]
Microcracking	Cracks form and propagate normal to or at an angle from the stress direction (similar to crack pinning).	-Favors small particles (d_p).	Evans and Faber [39] Oritz [40]
Cavitation	Ahead of the crack, dilation causes failure and void formation in the rubber/matrix interface.	-Interfacial bonding. -Rubber volume fraction (v_f).	Kinloch [41] Yee and Pearson [42]

According to Huang et al., matrix shear yielding is the predominant toughening mechanism accounting for 54–60% of the toughening at room temperature [29]. Shear yielding, shown schematically in Figure 5, is most effective in a ductile matrix, which can support high strains without brittle failure. The matrix ductility can be increased by incorporating chain-extending monomers—monomers with the same functionality of the base resin with larger distance between chain ends. The other key mechanisms enhancing fracture toughness occur because of the presence of low-modulus particle domains and include cavitation and particle yielding as 38% and 8%, respectively. Huang's results as a function of temperature are shown in Table 6. The table demonstrates the influence temperature has on the toughness mechanism that is activated. At low temperatures, near the T_g of the rubber, matrix shear yielding and rubber bridging account for all of the observed toughness. The loss of low-temperature toughness contributions from cavitation results from the increased rubber modulus at low temperatures, which favors interfacial debonding prior to particle tearing.

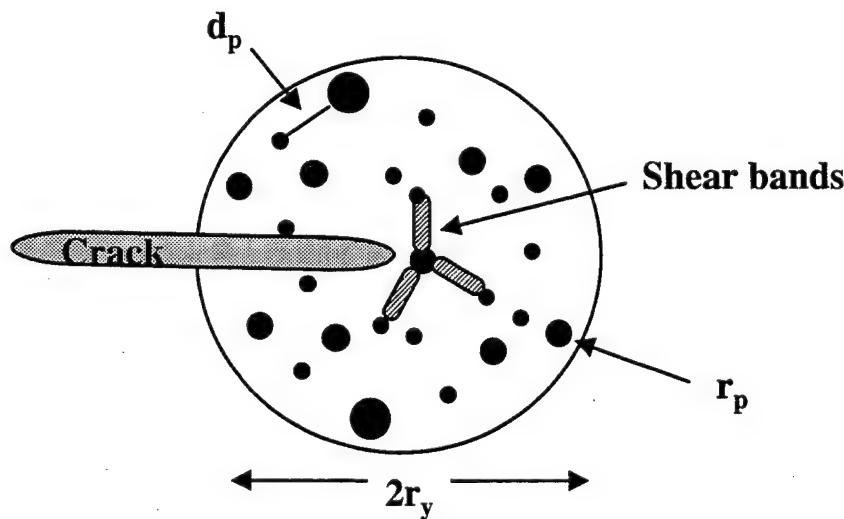


Figure 5. Shear Band Formation in a Toughened Thermoset. Shear Bands Form Ahead of the Crack Tip Due to Stress Concentration at the Particles in the Matrix.

The mechanism of failure in a matrix under various loading conditions is a key function in the selection of a toughening agent for a given application. However, other physical properties can be fundamental in the selection of a toughening agent. For instance, in cationic

Table 6. Approximate Contribution to Fracture Energy Based on Mechanism [28]

Mechanism	-60 °C	0 °C	23 °C	40 °C
Rubber Bridging	36%	14%	8%	5%
Rubber Cavitation	0%	29%	38%	48%
Matrix Shear Yielding	64%	60%	54%	47%

e-beam-cured resins, the catalyst-initiator is poisoned easily by the presence of amines. The amine functionality of typical CTBN rubbers prevents their use in toughening cationic resins [15]. Furthermore, second-phase tougheners require phase separation for maximum efficiency. The rapid cure of cationic resins under e-beam hinders the phase separation kinetics; thus phase separation is not readily observed.

The role of the rubber/matrix interface on the fracture toughness of modified plastics has been a controversial issue. The rubber/matrix interface can be varied in terms of interfacial bonding force, thickness, flexibility, and composition. However, it is difficult to assess exactly how changes in the interfacial region affect the toughness or the toughening mechanisms. The main toughening mechanisms operating in rubber-toughened epoxy are internal cavitation of the rubber particles and shear yielding in the matrix, which are believed to be promoted by interfacial adhesion [43]. It is evident that for cavitation to occur, the interfacial adhesion between the rubber particles and the matrix will have some impact on the toughness. Once adhesion is achieved above a level that prevents particle debonding and pull-out, further increases in the interfacial adhesion may induce alternate mechanisms of failure, thus decreasing the toughness.

4. Materials

The materials selected for the first phase of this adhesive development scheme are seq-IPN resins. The seq-IPNs are designed to be cured to ultimate strength in two stages—a thermal or room-temperature cure to green strength followed by an e-beam cure. Palmese et al. developed low-viscosity epoxy/acrylate and epoxy/methacrylate IPN blends for vacuum-assisted resin

transfer molding (VARTM) [44]—a technique that requires low viscosity (<500 cP) resins for composite processing. These seq-IPN resins exhibit low viscosity (200–800 cP), which optimizes their use in fiberglass composites by VARTM. Adhesives, however, are high-viscosity materials, and therefore the adhesive formulations described in this report are modified seq-IPN resins. The viscosity requirements for VARTM processing conditions are much different for adhesives; thus the material properties of the adhesives are unique to this class of material. A list of the common ingredients in both the adhesives and the resins is shown in Table 7; the purpose of key materials is briefly reviewed.

4.1 Epoxy-Amine Network - Thermal-Cured Compounds. The epoxides selected are Shell Chemical Company variations of the diglycidyl ether of bis-phenol A epoxide (DGEBA). The cure-kinetic, thermal, and mechanical properties of the diepoxide (EPON 828) reacted with the primary diamine bis(p-aminocyclohexyl) methane (PACM, Air Products) have been quantitatively characterized in a neat epoxy-amine network (represented in Figure 6) [45]. Variations of the network diepoxide structure have been evaluated to demonstrate the importance of chain architecture on toughness and glass transition temperature. Consequently, various molecular-weight DGEBA monomers (e.g., EPON 1001F, EPON 834) have been incorporated into the network synthesis to improve performance.

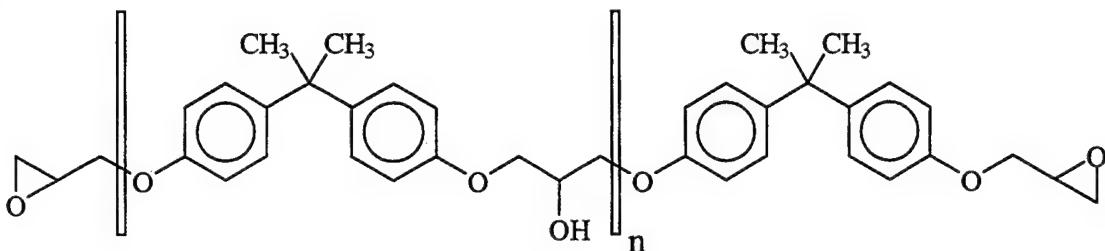
4.2 Methacrylate Network - E-Beam Compounds. As previously discussed, unsaturated alkenes are free radical cured on irradiation with e-beam. Thus, dimethacrylate materials are incorporated as the second stage of cure processing through e-beam for seq-IPNs. In order to prevent demixing of the monomers during storage and thermal curing of the epoxy-amine, resins with similar core structures (DGEBA and bis-GMA) are used; this selection is necessary to provide morphological control during network formation resulting in a homogeneous IPN. Methacrylated-DGEBA (bis-GMA), obtained from the reaction of bis-phenol A and glycidyl methacrylate, is a low-toxicity resin that is commonly used in dental adhesives [46]. 1,6-Hexamethylene dimethacrylate (HDDMA), on the other hand, is a difunctional alkene, which serves as a diluent and provides flexibility to the free radical network. In VARTM resins, the HDDMA is necessary to produce the low viscosity required for processing; in adhesive

Table 7. Examples of Monomer Components in E-Beam-Curable IPN

Chemical Name	Supplier	Principle Functionality	Purpose
HDDMA	Sartomer	Dimethacrylate	Diluent. Decrease viscosity during epoxy cure.
Bis-GMA	Sartomer	Dimethacrylate	Compatibilize methacrylate and epoxy networks.
PACM/PACM-20	Air Products	Difunctional primary amine	Aliphatic epoxy curing agent. Stiff-chain cross-linking of epoxy network.
EPON 828	Shell Chemicals	Diepoxide	Primary epoxy network resin.
EBECRYL 3605	UCB Radcure	Mixed epoxide and acrylate	Coupling between epoxy and acrylate networks.
EPON SU-8	Shell Chemicals	Multi-(Octa)-functional epoxide	Increase T_g of epoxy network (Novalac).
PGE	Shell Chemicals	Monofunctional epoxide	Terminating agent for epoxy network.
EPON 834	Shell Chemicals	Chain-extended diepoxide	Increase network flexibility/toughness.
EPON 1001F	Shell Chemicals	Chain-extended diepoxide	Increase network flexibility/toughness.
n-butyl methacrylate	Lancaster Synthesis	Monomethacrylate	Low volume-shrinking methacrylate.
ARL1	U.S. Army/University of Delaware	Mixed epoxide and methacrylate	Coupling between epoxy and methacrylate network.
ARL2	U.S. Army/University of Delaware	Mixed epoxide and methacrylate	Coupling between epoxy and methacrylate network.
ARL3	U.S. Army/University of Delaware	High functional mixed epoxide and methacrylate	Coupling between epoxy and methacrylate network.

formulations, HDDMA increases the tackiness of the uncured resin and provides a reduction in the T_g of the C-stage composite. The reduction in T_g allows high epoxide conversion (>95%) to be accomplished at low (<50 °C) temperatures. Further, resin tackiness is critical to the wetting

(a) DGEBA Monomer



(b) PACM Monomer



Figure 6. Chemical Structures for Epoxide Network Materials: (a) DGEBA Diepoxyde Monomer (EPON 828) and (b) PACM Diamine. The Average Distance Between Epoxides in the Diepoxyde Is Determined by the Average Number of Repeat Units (n) in the Monomer. Variation of 'n' Changes the Cross-Linking Density of the Network. EPON 828 Is n = 0.3 as Determined by HPLC. The Epoxide Equivalent Weight (EEW) of the EPON 828 Is 177; the Amine Equivalent Weight (AEW) of PACM Is 52.

of an adhesive. Improved surface wetting can be instrumental to improving bond performance on smooth surfaces.

4.3 Coupling Agents and Fillers. Coupling agents are used in seq-IPN formation in two key areas. First, because we are developing adhesive materials, the use of silane coupling agents improves adhesion to the oxide in metal (e.g., Al) lap shear evaluations. Most commercial adhesives utilize silane adhesion promoters because the thermal performance of the resin is maintained but bond strengths on metals are significantly improved [47]. Further, silane additives improve resin stability when inorganic fillers are incorporated. Network couplers are the second class of coupling agents incorporated in our formulations. Network coupling agents connect the methacrylate and epoxy networks through chemical bonds. Although acrylate couplers are commercially available, methacrylates with the desired structure are not

commercially produced. Consequently, partially methacrylated epoxide monomers were synthesized from various commercial diepoxides; the synthesis of example monomers as well as characterization is given in the Appendix. These materials have dual-functionality, epoxide and methacrylate, which allows them to chemically bond the two network materials together. The derived monomers are designated as ARL1(50) and like designations, where ARL1 designates the monomer repeat unit and (50) indicates the extent of conversion. We vary the conversion to have explicit control over the degree of network-network coupling. The synthetic method for generating methacrylates from epoxides was patented by Doyle et al. in 1967 [48]. A further discussion of materials used in this development is also presented in the Appendix. Chemical linking of the networks through the synthetic coupling materials (ARL1, ARL2, and ARL3) improves the thermal stability of the IPNs. Further, the epoxy-methacrylates serve to minimize load disproportionation into the networks and prevent phase demixing of the methacrylate/epoxy networks on a local level.

Other key components of the adhesive formulation include fill materials, which provide moisture resistance, improve high-temperature performance, and reduce costs. The fillers used in our formulations are silicate thixotropes, metal oxides, and pigments that improve handling of the paste adhesives. Commercial adhesives typically possess 30–70 weight-percent inorganic solids. In the development stage, we did not evaluate the impact of filler variations on performance; rather, we selected a minimum inorganic fill package to give efficient handling of the adhesive pastes.

4.4 Rubber Toughening. The seq-IPN resins discussed in the previous section are not effective adhesives because they lack critical toughness properties, causing poor performance under high stress and high load. Toughening of seq-IPNs is accomplished by using reactive rubbers (CTBNs) and reactive dendrimers (E1 and E2); the materials used in toughening studies are listed in Table 8. Upon curing the epoxy-amine network, the rubber or dendrimer becomes insoluble in the mixture and phase separates into discrete rubber domains. Although cure conditions can impact the formation of these rubber domains, we believe that the high concentration of diluent (>30% unreacted monomer) provides sufficient solvation of the C-stage

Table 8. Rubber Compounds Used to Toughen Epoxy/Methacrylate Seq-IPNs

ID	Content	Diluent	EEW(AEW)	Supplier
EPON 58003	18% ACN	Bis-phenol F	690	Shell
EPON 58005	26% ACN	Bis-phenol A	700	Shell
EPON 58006	18% ACN	Bis-phenol A	700	Shell
EPON 58034	18% ACN	Neo-pentyl-glycol (NPG)	275–305	Shell
EPON 58042	18% ACN	Cyclohexane-dimethanol (CDM)	340	Shell
Hycar 1300 × 8 (CTBN)	18% ACN	Carboxyl terminated	$M_w = 3550$	B. F. Goodrich
Hycar 1300 × 16 (ATBN)	18% ACN	5% n-aminoethyl piperazine (N-AEP)	~900	B. F. Goodrich
Hycar 1300 × 45 (ATBN)	18% ACN	<1% N-AEP	~1900	B. F. Goodrich
Hycar 1300 × 40 (ETBN)	18% ACN	Styrene	Not available	B. F. Goodrich
Hycar 1300 × 44 (ETBN)	18% ACN	None	$M_w = 3900$	B. F. Goodrich
Boltorn E1	$M_w = 10\text{ k}$	None	830 (11/mol)	Perstorp
Boltorn E2	$M_w = 12\text{ k}$	None	375 (30/mol)	Perstorp
TPA-1	6-μm Core	Powder	Not reported	Applied Poleramic, Inc.

epoxy network to allow equilibrium rubber phases to form under ambient cure conditions. The impact of cure temperature and cure rate for the epoxy-amine network is evaluated later in this report. The CTBN loading that provides optimization of toughness is between 8 and 12 weight-percent and results in a two-fold increase in fracture energy and LSS. Greater than 20% rubber loading results in the formation of a co-continuous network of seq-IPN epoxy and rubber, producing a material with poor high-temperature performance. Dendrimer materials are designed to provide optimum toughness of epoxy networks at 6–12 weight-percent additions; we did not observe any deviations from this operation window for seq-IPNs.

Although composition of adhesives varies, a typical formulation for a toughened paste is shown in Table 9; the two-part paste composition shown is mixed using either an amine or amine adduct (Part B) in stoichiometric equivalence.

Table 9. Typical Formulation for a Typical Seq-IPN Adhesive Paste

Material Component	Composition (phr)
Amine (PACM)	36
Diepoxides (DGEBA)	100
ARL1 (MEMM)	56.7
CTBN	35.5
Bis-GMA	106
HDDMA	36.7
Cabosil (thixotrope)	3.7

5. Seq-IPN Resins

The processing method for epoxy-amine reactions can dramatically impact the cured resin properties. For example, the glass transition temperature of the final composite shows a strong dependence on the stoichiometry and extent of cure of the epoxy-amine network [45]. We selected experimental cure parameters that optimize the cure of the epoxy-amine network. Phase separation of CTBN rubber occurs completely for the toughened systems, which we evaluated.

The rate and extent of thermal cure of the epoxy-amine network has a strong dependence in viscosity, which is dependent upon the initial monomer ratios. For example, a toughened adhesive formulation containing 20% (w/w) rubber is 10% more viscous than the untoughened equivalent system. However, both formulations reach full network conversion at C-stage in the presence of diluents [49]. We follow the cure conversion using transmission Fourier transform infrared (FTIR) on representative adhesive samples. A similar cure study was performed by Dalal and Palmese for VARTM resins [50]. However, the kinetics for adhesive cure are dramatically slower as a result of much lower diluent concentrations (higher viscosity). From

the FTIR cure analysis, a thermal processing window is determined. Future efforts will investigate step-cure process cycles for optimizing cure rate. For this study, we merely established the time required to completely react the epoxide and amine. The complete cure is necessary to ensure reproducibility of the thermal and mechanical properties of the samples.

Side reactions between the components in these IPNs may be a concern. Dalal and Palmese evaluated the reactivity rates of acrylates and methacrylates with a primary amine (PACM) and observed that both acrylates and methacrylates compete with the epoxide for reaction with the amine moiety [50]. An acrylate combines with an amine through a Michael's addition across the C = C bond, while an epoxide reacts with an amine in the traditional ring-opening nucleophilic substitution. The occurrence of an amine-acrylate reaction complicates control of the network structure and decreases epoxide-amine conversion. However, the Michael's addition product of the PACM primary hydrogen (1H) with bis-GMA methacrylate at 70 °C occurs an order of magnitude more slowly than the DGEBA-PACM(1H) reaction. Consequently, methacrylated monomers improve control of the network structure. Methacrylated monomers also have a reduced cure shrinkage compared to acrylates and are therefore ideal for adhesive development.

5.1 Kinetics and Extent of Cure. FTIR spectroscopy was used to monitor changes in the fingerprint spectrum of the monomer blends (1,700–600 cm⁻¹). The intensity of infrared (IR) active modes for epoxides, amines, and methacrylates was monitored at room temperature, 50 °C, 65 °C, and 80 °C, to determine time to cure. Among the IR vibrational modes that occur in the fingerprint are the epoxide ring stretch (912–920 cm⁻¹), the C = C symmetric (1637 cm⁻¹) and -CH out-of-plane (945 cm⁻¹) stretches of the methacrylate, and the *para* di-substituted benzene breathing mode (1,510 cm⁻¹) [51]. In our analysis, we used integrated peak intensity for quantitative analysis, since these measurements were not suspect to baseline drifts associated with the continuing reactions. The epoxide and methacrylate modes were used to determine degree of reaction and to observe any side reactions. The di-substituted benzene ring-breathing mode is unaffected by the chemical reactions and was used as the internal standard for normalizing spectra to a constant molecular concentration, which allows the cure to be evaluated linearly with time as per the Beer-Lambert Law.

Having selected the molecular modes for evaluation of chemical cure, we established the dependence of network cure rate on temperature of cure for a toughened and an untoughened system with low methacrylate concentration ($\phi_{\text{ma}} = 0.25$). The result of one study is shown in Figure 7. Figure 7 plots the extent of conversion of epoxides (ξ), measured using the epoxide ring stretch ($\nu_{\text{max}} = 916 \text{ cm}^{-1}$), as a function of cure time at 50 °C for both rubber-toughened and untoughened seq-IPNs. The effect of toughening on epoxy network cure rate is measured as lag time ($t_f - t_u$) and increases with the extent of cure (shown in Table 10). The results are as expected—the rubber phase separates on thermal curing, increasing the viscosity and decreasing the diffusion rate for the reacted amine. The average cure time is 50% longer at $\xi = 0.5$ as a result of the CTBN. Whether the decrease in thermal cure rate on toughening results from the phase segregation of the rubber, which immobilizes partially reacted amines, or from the increased viscosity of the system has not been determined. The lag time for cure is maximum for high-epoxy (>70% epoxide-amine) systems. When the concentration of diluent methacrylates is high (>40%), the cure variation between toughened and untoughened systems is negligible.

The cure conversion of epoxy-amine, as shown in Figure 7, demonstrates three key features associated with the epoxide and amine reaction. At very short times (<90 min), the conversion rate proceeds rapidly to approximately 45% in both the toughened and untoughened systems. This rapid-cure stage occurs because the primary amine (R-NH₂) is very reactive and the mobility of PACM is high. Once the primary amine, PACM(1H), has reacted, the cure rate slows dramatically as a result of a decrease in PACM mobility—steric hindrance from an increase in network (and amine) molecular weight—and a decrease in amine reactivity for the secondary amine (R₂-NH). After about 10³ min, the signal for the epoxide mode has diminished sufficiently to make quantitative measurement difficult; the measurement error makes determination of a crossover in the two samples impossible using this technique.

The impact of cure temperature on the rate, extent, and homogeneity of the epoxide-amine reaction was evaluated for a toughened adhesive formulation. The sample adhesive formulation from Table 9 is evaluated as a function of cure temperature from room temperature to 80 °C. The results are presented in Figure 8. The conversion as a function of time at 50 °C is much

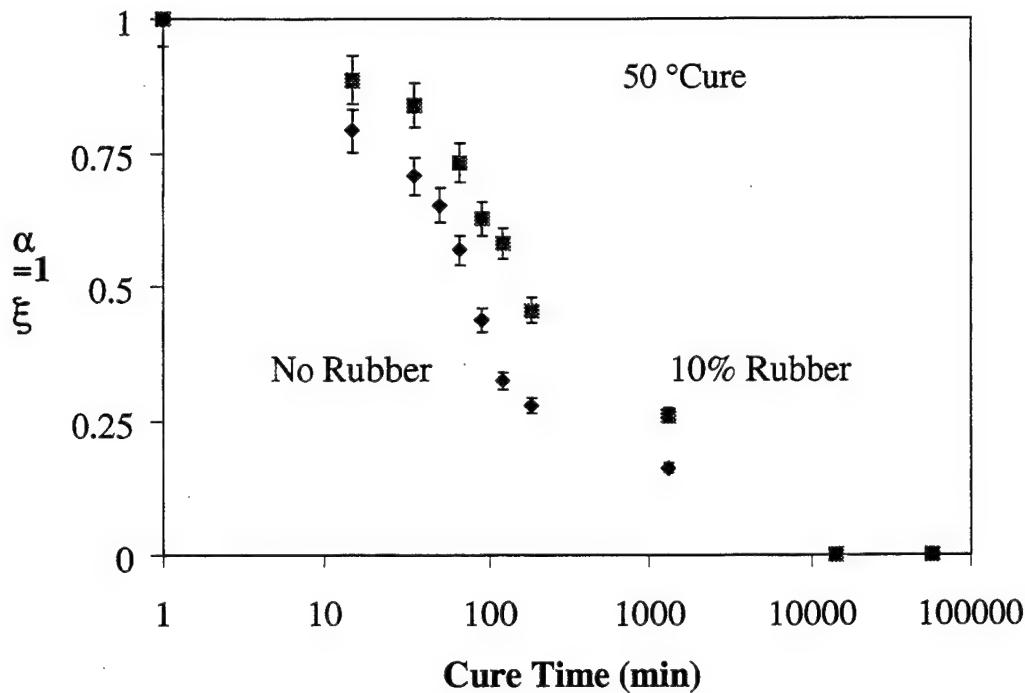


Figure 7. Cure Kinetics for Two Seq-IPNs ($\phi_{ma}=0.25$) Showing the Extent of Cure of the Epoxide-Amine Reaction With Time for Samples Cured at 50 °C. The High Viscosity of the CTBN Toughening Additive Has a Significant Impact on the Kinetics of Cure in These Systems. From These Results, Long Cure Times (>1000 min) Are Necessary to Achieve Complete Network Conversion.

Table 10. Cure Lag Time Between Toughened (t_t) and Untoughened (t_u) Adhesives for $\phi_{ma} = 0.25$

Conversion (ξ)	Lag Time ($t_t - t_u$) (min)
0.8	35
0.65	40
0.45	90
0.2	900

faster for ADEP-01 than for the example formulation shown in Figure 7. This is a result of the increased methacrylate (diluent) concentration ($\phi_{ma} = 0.45$). The key stages of cure development—PACM(1H), PACM(2H), and vitrified limit—are observable for all four cure cycles shown in Figure 8. As a function of cure temperature, the high-temperature cure (80 °C)

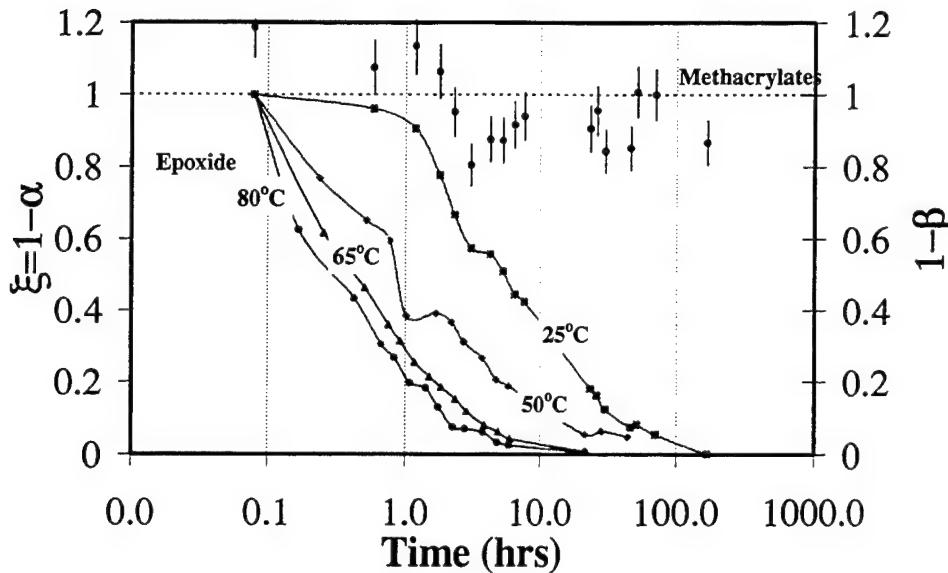


Figure 8. Extent of Epoxide Conversion as a Function of Time at Key Processing Temperatures for Adhesive Pastes. The Cure Rate Is Significantly Increased for Processing at 50 °C Compared to Room Temperature. In the High-Temperature Cure Study (80 °C), the Michael's Addition Reaction Does Not Occur to an Appreciable Extent for Methacrylates ($\nu = 1637 \text{ cm}^{-1}$) as Demonstrated ($1-\beta \approx 1$).

provides the optimum preparation rate ($t_{\text{cure}} < 3 \text{ hr}$); however, the Michael's addition reaction warrants consideration at this temperature. One advantage to monitoring extent of cure by epoxide conversion is that amine, which may react through Michael's addition, is not included in the measurement. The methacrylate conversion at 80 °C ($1-\beta$) is plotted in the figure as well and does not appear to diminish in any correlated fashion with epoxide concentration. Therefore, we conclude that the network structure is >90% epoxy-amine, and the extent of cure reaches >90% conversion at long cure times or high cure temperatures.

Although high cure temperatures may not be reasonable for field use of these materials, the rapid curing of materials is desirable for testing purposes. In order to balance cure testing with a feasible field-use cycle and to reduce the probability of PACM(1H) with methacrylate reactions, a processing condition involving 50 °C cure for 2–3 hr followed by a post-bake of 80 °C for 1–2 hr or 50 °C for 10–12 hr was selected. This processing condition assures complete reaction of the epoxides and minimizes the time required to cure the samples. The impact of this process

condition on phase separation of the rubber particles has not been fully characterized; however, initial measurements by Scanning electron microscope (SEM) indicate a homogeneous distribution and similar particle size ($\sim 5\text{--}8 \mu$) irregardless of processing temperature. We believe that the rubber particle size is locked in at the time of gelation in the system or that particles reach an equilibrium size after thermal cure due to the low T_g of the C-stage network ($T_g[\text{green}] = 20^\circ\text{C}$ by DSC).

5.2 Thermomechanical Characterizations. The thermochemical and thermomechanical properties of the seq-IPNs are characterized by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). The resin DMA- T_g is reported as the maximum in the loss modulus (E''). Two heating rates are used for DMA measurements. At low temperatures (-100 to 25°C), a heating rate of $1^\circ\text{C}/\text{min}$ is used with a sampling frequency of 0.1 Hz allowing separation of the rubber T_g from the bis-phenol A (BPA) β -relaxation. Above room temperature, the matrix T_g is measured from 25 to 200°C using a ramp rate of $5^\circ\text{C}/\text{min}$ and 1-Hz frequency. DSC measurements are usually performed using a temperature ramp of $10^\circ\text{C}/\text{min}$; however, 2 and $5^\circ\text{C}/\text{min}$ are used for C-stage T_g measurements because the transition is small and broad. DMA and DSC T_g 's usually agree to within 5°C , which is well within the expected error of the techniques.

The DMA results for a series of epoxy-amine/acrylate seq-IPNs that are toughened using CTBN and chain extenders in varying amounts are plotted in Figure 9. Clearly, the DMA- T_g of the materials does not change significantly ($99^\circ\text{C} < T_g < 105^\circ\text{C}$) for these systems, even though a high loading of rubber (20%) and chain extenders (20%) are presented. Consequently, we can conclude that CTBN is successfully phase separated from the seq-IPN matrix. A DMA analysis of samples, which were C-stage but not e-beam cured, shows that the phase separation occurs during the thermal processing of the adhesives. Once formed, the rubber particles do not negatively impact the thermal performance. Low-temperature DMA plots showing the presence of phase separated rubber domains after e-beam cure are shown in Figure 10. The β -relaxation of bis-phenol A was separated from the rubber relaxation by using the 0.0 high energy (HE) frequency.

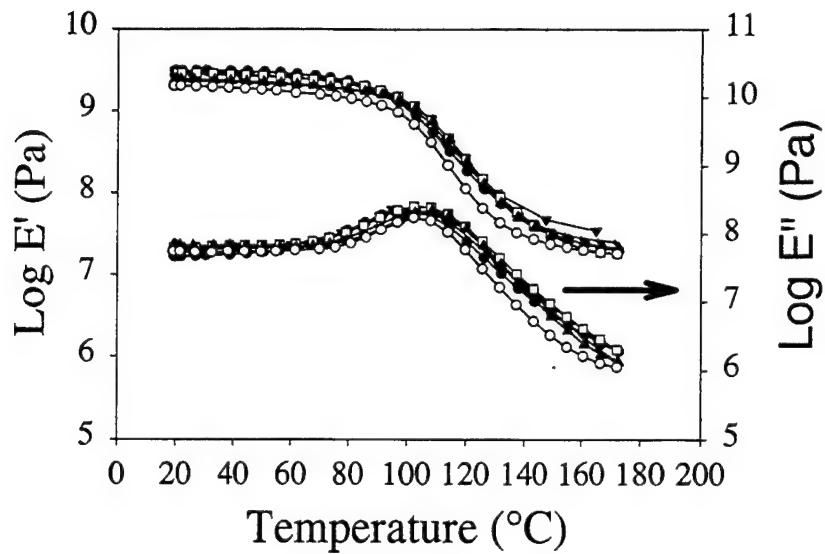


Figure 9. DMA Plot for Storage and Loss Modulus of a Series of Rubber-Toughened Seq-IPNs Formulated From Epoxy-Amine and Acrylate Functionality. The Maximum in the Loss Modulus Is Reported as the DMA-T_g. Because the Rubber Phase Separated From the Matrix on Curing, the T_g of the Materials Is Not Affected by the Addition of Rubber and Chain Extenders.

5.3 Phase Separation of CTBN. The preferred method of toughening seq-IPN adhesives has been to use thermodynamic phase separation during the C-stage formation of the adhesive bond, a method synonymous with thermoset epoxy network toughening. The best performance in epoxy adhesive toughness is achieved using functionalized CTBN rubbers that co-cure with the epoxy-amine to form bonded rubber particles. The results for seq-IPN analysis are consistent with the literature reports for thermoset epoxy materials in that small rubber concentrations (<20%) induce discrete rubber particles (0.2–5 μ m), while large concentrations of rubber form a co-continuous morphology. The rubber particles improve toughness by changing the energy absorption of the matrix and inhibiting premature failure of the thermoset, which often results from small defects.

Alternatively, the second phase is added as rubber or thermoplastic particles. The size, surface reactivity, and concentration of the particles greatly influence the toughness for the thermoset. Often, the surface of the particles is coated with an adhesion promoter to enhance the interaction between the thermoset and the filler. Generally, the addition of discrete particles for toughening is less effective than the addition of reactive rubbers. We expect to explore the

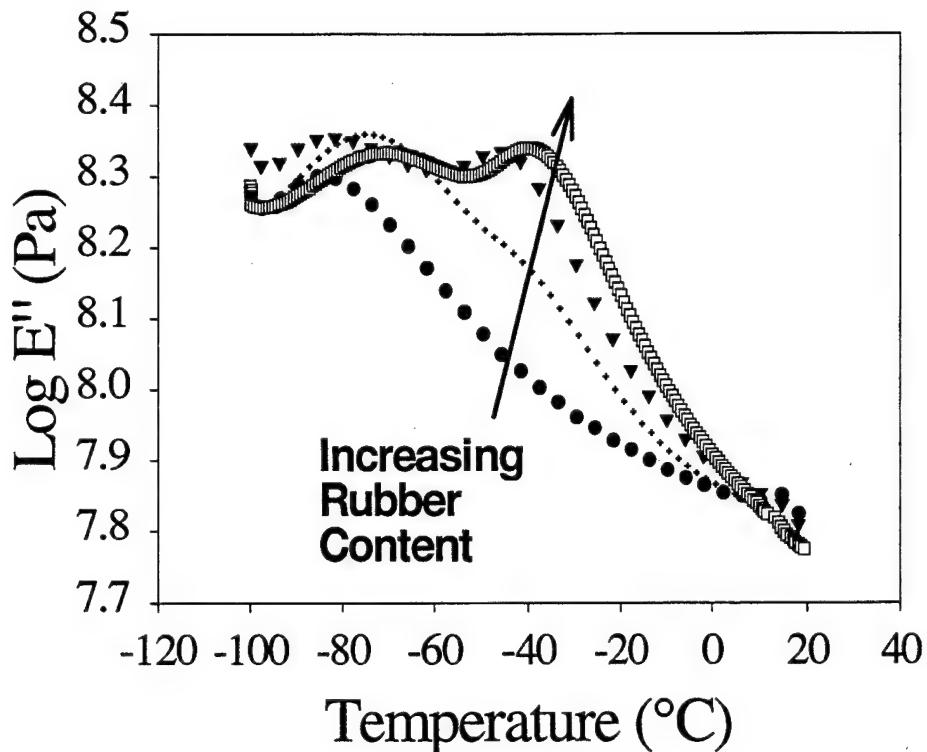


Figure 10. Low-Temperature DMA- T_g Analysis for Rubber-Toughened Seq-IPNs. Increasing Rubber Concentration Results in Larger Rubber Domains, Which Increases the Sensitivity of DMA to Detection. However, Rubber Domain T_g Transitions ($-50^\circ\text{C} < T_g < -38^\circ\text{C}$) Are Evident, Even at Low Rubber Loading, Which Supports the Proposal That Phase Separation Occurs in These Matrix Systems. The Bis-Phenol A β -Relaxation Is Also Resolved ($-90^\circ\text{C} < T_\beta < -70^\circ\text{C}$).

influence of dispersed material toughening agents in developing one-part and film-type adhesives for e-beam cure where the kinetics of curing occur too quickly to allow phase separation. For two-part paste adhesives, however, the results from the addition of rubber-toughening agents has already given promising results and will be the method in further development work.

The second method of toughening thermosets is to add chain extenders to the network. The average distance between cross-links is a key parameter governing the toughness of the network. By varying the spacing of cross-link sites in the network, through n-MER addition of the base resin (oligomers), the average number of cross-links per unit volume is reduced only slightly,

while the distribution of cross-link sites is increased. This provides greater flexibility to the network, although usually at the expense of the T_g .

The consequence of phase separation of the rubber domains was carried out to create a phase map of the rubber in both one-part and two-part adhesives. Because the system being studied is quite complex, the experimental phase diagram was developed by assuming that like-functional monomers are equivalent in the phase envelope. Thus, methacrylates, bis-GMA and HDDMA, comprise one axis of the phase diagram, while the epoxy-amine matrix comprises a second axis. To produce a ternary phase diagram, the rubber is plotted along the remaining axis.

As is shown in Figure 11, phase separation, as determined by the optical cloud point, occurs over a wide range of experimental conditions. However, at high methacrylate concentrations, the rubber phase does not form a dispersive second phase. From visual evaluation, samples with high methacrylate concentrations will not show significant increases in toughness but will show a decrease in glass transition temperature. The fact that high concentrations of methacrylate inhibit rubber phase separation was verified by a decreased T_g of the toughened samples. When phase separation was not obvious, matrix T_g 's were suppressed by as much as 20 °C, while in the multiphase epoxy/rubber samples, T_g 's decreased by only 2–5 °C (see Figure 9).

5.4 Microscopy. In rubber-toughened epoxy-amine networks, the cure temperature and cure rate have a significant impact on the formation of the CTBN phase. The rubber phase in epoxy-amine networks forms under a kinetic constraint that is mitigated by a physical limit at gelation or vitrification. In seq-IPNs, however, phase separation of the rubber occurs in the presence of a high concentration of diluent. Diluent methacrylate or acrylate monomers impact the viscosity profile of the adhesive such that uniform particle sizes are formed under all observed experimental curing conditions. The size of the domains is dependent only on the concentration and composition of the CTBN. SEM was performed on a number of test specimens to determine morphology, including particle size, and to estimate failure mechanisms of the materials. SEM results for mixed epoxy/acrylate systems are in agreement with DMA studies and demonstrate that particle phase separation forms uniform domains. The concentration of rubber was compared with the literature values of particle sizes for

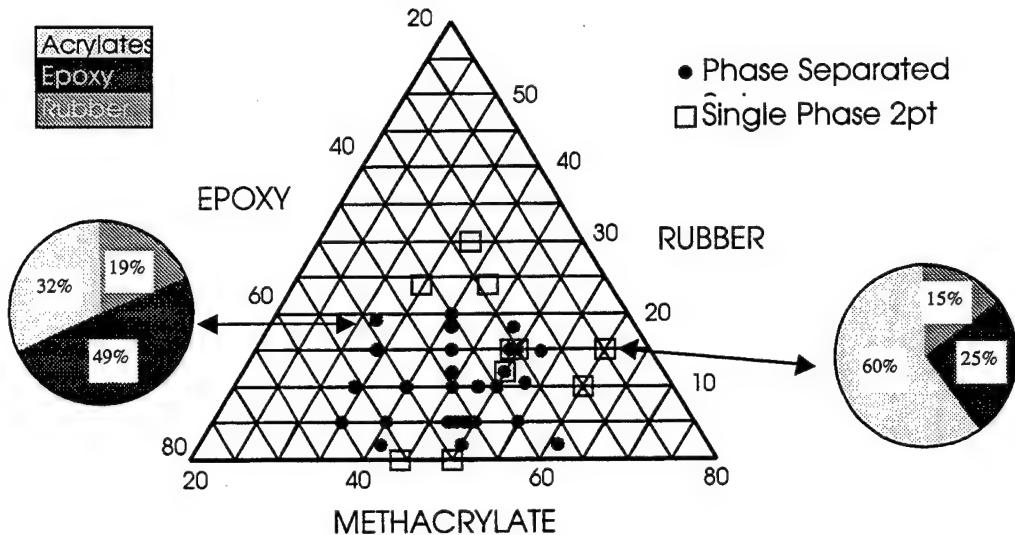


Figure 11. Phase Diagram From Experimental Evaluation of Epoxy/Methacrylate Blends Cured to C-Stage at 50 °C for 24 hr. The Optical Cloud-Point Was Determined as an Indication of Phase Separation in These Results. Particle Sizes Must Be Large Enough to Scatter Visible Light in Order for Phase Separation to Be Evident by This Method.

rubber-toughened epoxy networks [52–54]; our results are consistent with literature for particle sizes. SEM was performed on Au-Pd-coated (5–7-nm thickness) fracture specimens. Figure 12 shows an example fracture surface for a toughened seq-IPN with 5% CTBN. The average hole size is about 5 μ .

5.5 Fracture Toughness. The second method used for screening adhesives is the fracture toughness of the resin [55]. Fracture toughness measurements for a number of epoxy/acrylate materials were performed under the initial development of adhesive paste resins. We explored the same parameters, impact of chain extender and rubber concentration, and their effect on toughness. Additionally, we included an evaluation of the effect of seq-IPN compositions on the toughness of the resins (e.g., the concentration of epoxy-amine to acrylate or methacrylate). The impact of network compositions is more difficult to assess by lap shear measurements because of the variation in material viscosity with resin composition. The fracture toughness, or K_{IC} , is a measure of the matrix ability to resist fracture. Some K_{IC} results are plotted in Figures 13 and 14.

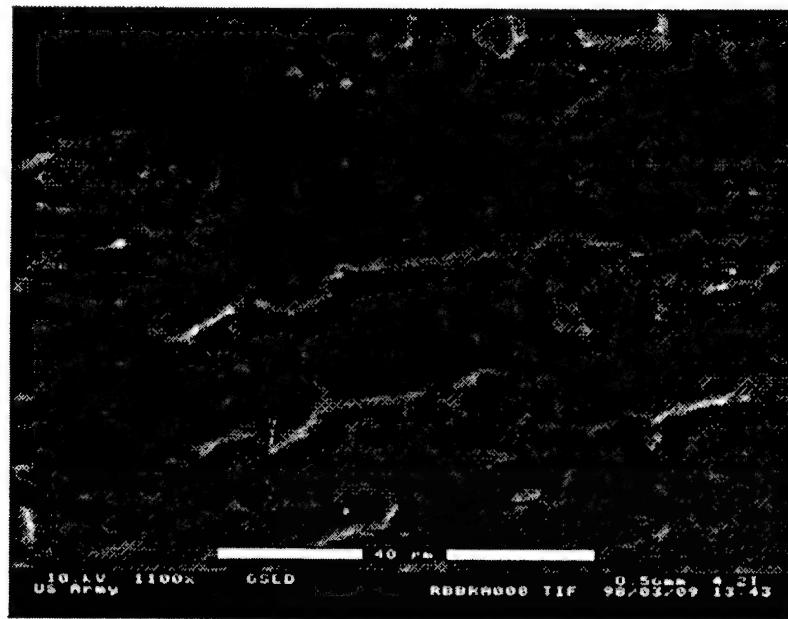


Figure 12. SEM Micrograph of a Rubber-Toughened (5% CTBN) Seq-IPN Fractured Rapidly. The Example Shows Evidence for Failure Modes Involving Matrix Yielding, Cavitation, and Particle Tearing.

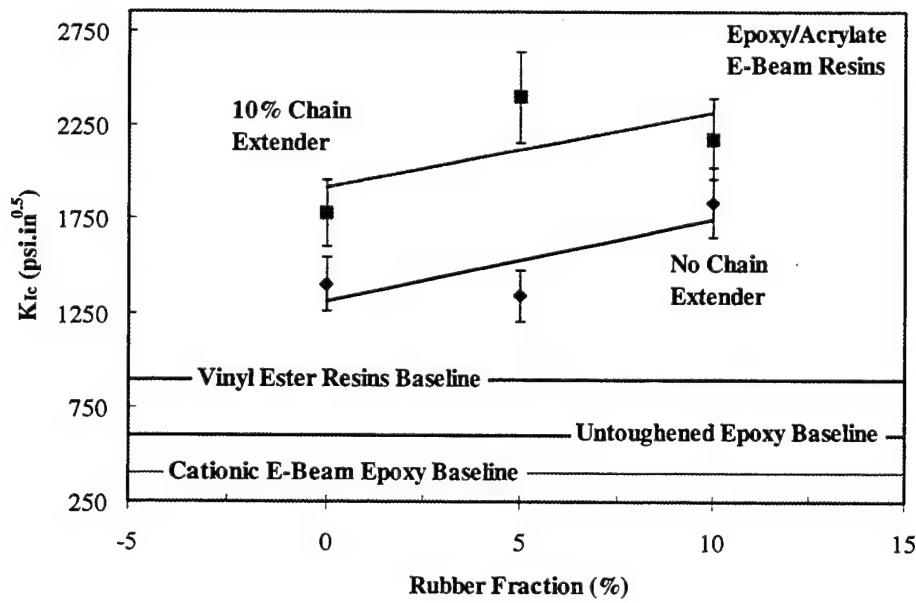


Figure 13. K_{IC} Results From Experimental Evaluation of Adhesive Paste ADEP01 Type Formulation Using EPON 58006 Rubber and EPON 834 Chain Extender.

Figure 14 demonstrates the impact of the network composition on the fracture toughness of the material. Acrylates, which exhibit a significant volume shrinkage on cure, increase the average stress in the matrix when used in increasing concentration. Further, the CTBN is designed for use with epoxy-like materials. Thus, rubber phase separation does not occur as effectively from the acrylate as the epoxy; the rubber has an increased compatibility with the acrylate. The T_g of the high-acrylate systems are significantly reduced compared to the low-acrylate networks, in part, because of the less efficient phase separation occurring when rubber materials are added to toughen the network. The dilution of the network structure with long-chain rubbers decreases the cross-link density and, therefore, results in a lower T_g . Two other key observations from the figure is that the fracture toughness does not appear to be greatly affected by rubber concentration and that fracture toughness levels off below 40% acrylate. This second observation would indicate that an e-beam adhesive is best formulated with an acrylate concentration less than 40 phr to achieve optimum fracture toughness.

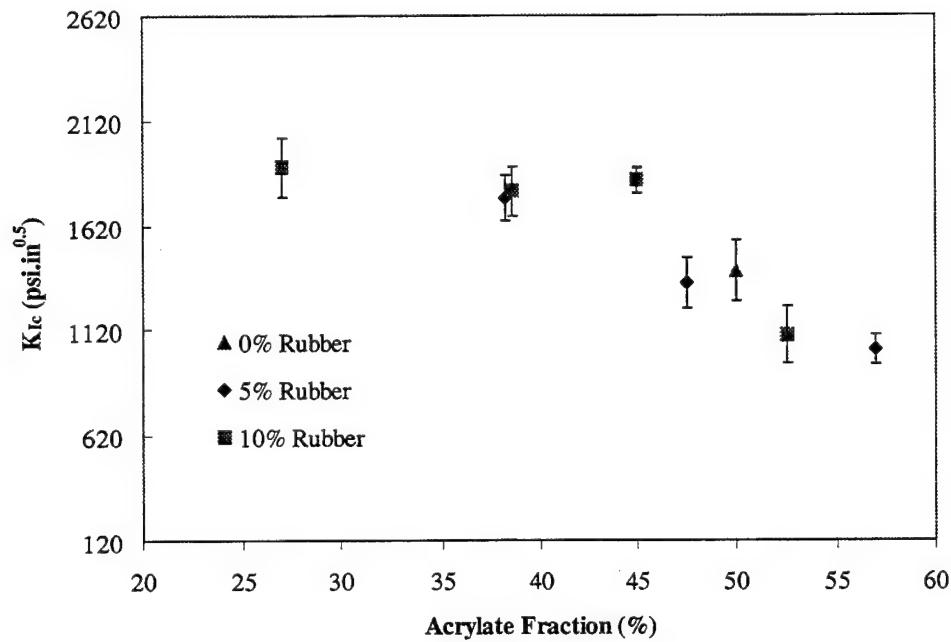


Figure 14. Impact of Methacrylate Concentration on Fracture Toughness of IPNs. High Acrylate Concentrations Result in an Increased Residual Strain in the Matrix Material, Which Decreases the Influence of Toughening Agents. Highly Strained Systems Are More Difficult to Toughen.

6. Seq-IPN Adhesives

Mechanical tests were performed using the ASTM standard for fracture toughness [55] and for LSS [56]. Both single-edge notch band (SENB) and lap-shear measurements are performed using a 1-mm/min loading rate.

As with epoxy networks, the seq-IPNs from EPON 828-PACM/methacrylate are brittle. Consequently, unmodified seq-IPNs are inadequate for adhesive application just as epoxy systems. However, seq-IPNs demonstrate a higher baseline toughness than epoxy materials formulated from the same epoxide-amine combination. Improving the toughness of seq-IPN blends is key to creating an alternative cure adhesive by this approach. The 1992 ORNL CRADA demonstrated the challenge in toughening e-beam resins, especially cationic epoxy resins. Recent characterizations of cationic-cured e-beam systems showed that toughness is not achieved using traditional methods used in epoxide-amine systems, such as CTBN and chain-extender additions, because of catalyst poisoning. However, seq-IPN cure through similar chemical mechanisms to epoxy-amine and free radical systems and should therefore be effectively toughened using traditional methods.

Because they are often unsupported and located at interfacial junctions, adhesives experience a larger apparent load than the resin in a composite [47]. Consequently, adhesives require higher strength and stiffness. Further, because of the mixed Mode I/II stresses experienced in adhesive loading (e.g., under lap shear conditions), high peel strength and ductility are also necessary. The peel strength is directly proportional to toughness, which is a measure of the ability of the adhesive to absorb energy during loading. In the development of candidate adhesive materials, we use simple screening techniques, such as LSS and fracture energy, to evaluate the impact of toughening on adhesive performance. The challenge of toughening the matrix without diminishing thermal stability (e.g., glass transition temperature) remains key to adhesive development [55–58]. We have already demonstrated that toughened systems maintain their thermal stability, and we will now observe the effect of toughening on adhesive strengths.

The LSSs of some adhesive formulations are listed on 3501-6 carbon fiber composite panels in Tables 11 and 12. Prepared samples were tested as both green and fully cured adhesive specimens. Table 11 contains the experimental results for double-notch (DN) LSSs. From our initial experiments, we determined that bond strengths using DN testing on composite panels would not allow us to reach ultimate strengths of the adhesives due to premature interlaminar failure of the composite (EA9394 failed by interlaminar peel). The T_g for each of these adhesive samples was measured using DSC, and the results are listed in Tables 11 and 12. The target T_g of a 120 °C (250 °F) adhesive is well within the scope of this effort.

Table 11. Double-Notch (DN) Lap Shear Results for Composite Panels. Composite Interlaminar Failure Occurred at Very Low Values, Which Is Believed to Result From the Preparation Methods Used in the DN Geometry.

Sample ID	Bond Strength (psi)	DSC- T_g (°C)
JDW62 (two-part)	2000±200	120
JDW63 (two-part)	2300±280	121
JDW73 (one-part)	1550±200 ^a	90 ^b
JDW74 (one-part)	2000±300	88 ^b
DEXTER HYSOL EA9394	3200±300	78

^a Sample failed in the bond-line.

^b Epoxy network not fully cured (FTIR).

Table 12. Initial LSSs for IPN Paste Adhesives on Composite Finger Specimens (ASTM D 1002). All of the Full Cured Seq-IPNs Produced Composite Interlaminar Failure.

Sample ID	Bond Strength (psi)	DSC- T_g (°C)
SHM1FA (two-part, full cure)	2900±400	120
SHM1FA (two-part, epoxy-amine cure/no EB)	1100±100	30
SHM2B (two-part, full cure)	2750±400	121
SHM2B (two-part, epoxy-amine cure/no EB)	600±100	(20)
SHM3FA (two-part)	3100±300	120
SHM3B (two-part)	3400±400	121
DEXTER HYSOL EA9394	3700±300	78

From finger-joint lap-shear measurements on 3501-6 composites, we determined that the bond strengths of the e-beam paste adhesives exceed the test limit for the composite. We observed composite failure (stock break) in all of the e-beam-cured two-part adhesives. One-part seq-IPN paste and film adhesives did not exhibit high LSSs. For example, JDW73, an untoughened one-part paste adhesive, and JDW74, the toughened film adhesive, are 40% as effective bonding agents than two-part pastes. The impact of toughening in JDW74 is represented by 33% higher LSS than JDW73, neglecting error analysis. Phase separation is evident in both one- and two-part systems by formation of an opaque adhesive film on epoxy-amine cure. As a note, the two-phase morphology for the one-part adhesive appears to be temperature sensitive; the opacity increases with increasing temperature, which is consistent with a lower critical solution temperature (LCST) condition. The implication of LCST phenomena is that the one-part materials are in a realm of metastability, implying that controlling particle size after e-beam cure will be a challenge using this approach.

After the evaluation of performance for the samples shown in Tables 11 and 12, we modified the base resin formulations to improve control of network architecture and induce rubber phase separation and tested the modified adhesives on 1-in \times 4-in \times 0.062-in 7075 T6 al substrates. The results are presented graphically for unfilled and unsupported two-part adhesive pastes in Figure 15. The data show a significant spread in measured LSS for each formulation, which is indicative of the need to further improve matrix toughness; however, the scatter in ADEP01 (JMS6) has been correlated with a variation in e-beam cure and a corresponding variation in T_g . We assessed a typical toughness trend using the average LSSs. We are encouraged by the results from ADEP01 where the highest LSSs are >6000 psi. This sample also exhibits a T_g of 123 °C. LSSs of this degree are exceptional for an e-beam-cured adhesive and are comparable to the best aerospace film adhesive (CYTEC FM73 and Dexter Hysol EA9628). We believe that some of the variability in LSS results from bond-line thickness fluctuation in addition to network cure variation and adherent notch sensitivity in these resins. We will evaluate the impact of these variables as we continue to improve the properties of the adhesives. Control of adhesive thickness will be addressed using both nonwoven scrim cloth and/or alumina-silicate microballons.

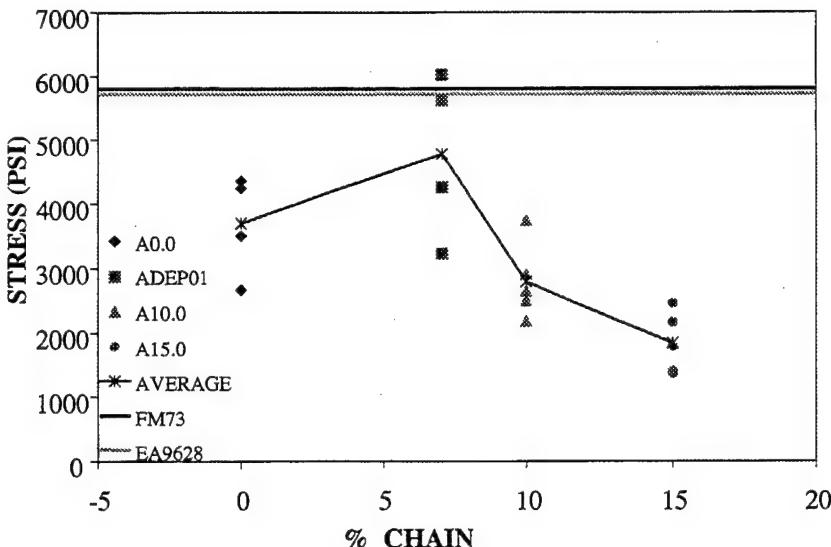


Figure 15. Effect of Chain-Extender Concentration (EPON 834) for 10% CTBN-Filled Seq-IPNs on the Al LSS. The Variation in LSS for ADEP015 Is Directly Correlated With a Degree of Cure in the Network. T_g Is Greatest for the Fully Cured Samples, Which Also Exhibit the Highest LSS.

Despite the variability in these initial experiments, we are confident that our approach to designing an e-beam adhesive, which introduces toughness through key energetic absorption modes, such as matrix shear yielding and rubber particle cavitation, will provide a rapid optimization of the adhesive LSS while maintaining high thermochemical stability. The untoughened adhesives, AD, fail at 40% of the LSS of the toughened adhesives (50% of the maximum LSS of ADEP01). We accomplished this improvement in toughness without diminishing the thermal stability from the base adhesive formulation ($T_g > 120$ °C). From Figure 15, it is also clear that the extent of toughening achievable in a 10% CTBN-modified seq-IPN adhesive, though network design is limited by the extent of chain-extender loading. Presumably, this limitation results from particle-size variations in the rubber at high chain-extender concentration.

The results in Figures 13 and 16 demonstrate a direct correlation between the fracture toughness of the matrix resin and LSS performance of an adhesive. Clearly, the ability for the matrix to absorb energy (e.g., through shear yielding) results in a higher K_{IC} and an equally improved LSS. By comparing these data sets, the mode of failure in the adhesive lap shear can

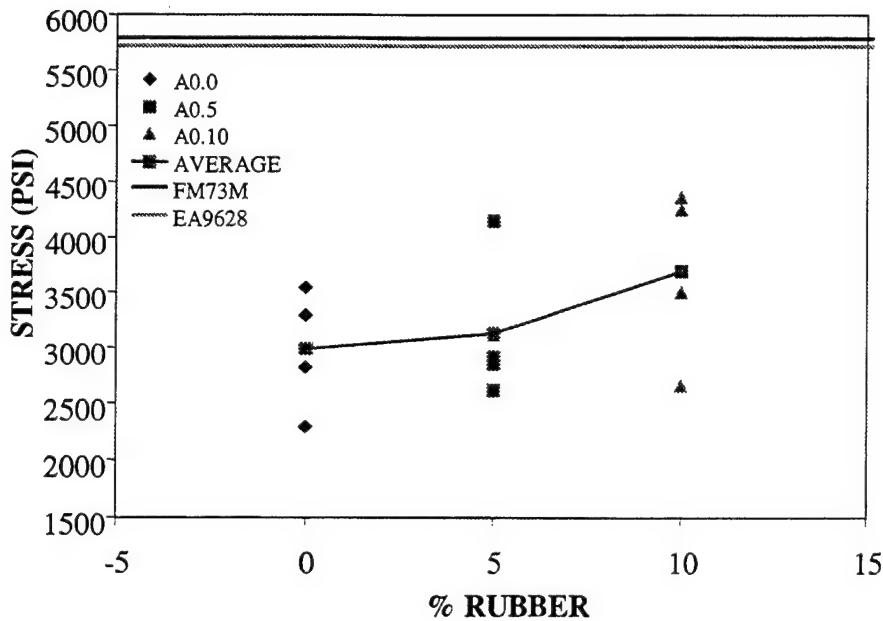


Figure 16. Effect of Rubber Concentration on the Toughness of Adhesive Pastes Evaluated Using Al-Al Lap Shear Techniques on Finger-Joint Samples. In Conjunction With the Results From Figure 15, the Best Toughening Is Achieved by Using Rubber and Chain Extenders to Produce a Matrix Network Capable of Shear Yielding as Well as Rubber Cavitation.

be correlated to the ability of the matrix to shear yield. The initial evidence demonstrates the importance of designing a matrix resin for the adhesive that minimizes the cross-link density of the matrix—maximizes the flexibility of the matrix—without diminishing the network integrity or T_g .

LSS results for our best toughened adhesive, ADEP01, are shown for 2024 T3 Al-Al and IM7/977-3 composite-composite substrates in Table 13. Also listed in the table is the average displacement on failure for lap-shear measurements. Displacement can be used to qualitatively compare toughness in addition to load at failure. Larger displacement is usually associated with higher toughness, although displacement may not scale directly with maximum load. The e-beam-cured adhesive paste, ADEP01, is a strong candidate for aerospace and Army applications. The comparison is shown for CYTEC's FM73 film adhesives on the same substrates because FM73 is among the best adhesive materials available. However, FM73 has an

Table 13. Results From CAI Study of Adhesive Pastes on Aluminum (2024 T3) With CYTEC BR 127 Primer and Composite (IM7/977-33) Fingers. Sample Overlap Dimensions Are 0.5 in × 1.0 in.

Aluminum Lap Shear Sample ID	Average Load (psi)	Average Displacement (in)
ADEP01	4760±900	0.060
ADEP01 (postbake 150 °C)	4000±200	0.049
FM73	6370±90	0.115
Composite Lap Shear Sample ID	Average Load (psi)	Average Displacement (in)
ADEP01	4850±700	0.095
ADEP01 (postbake 150 °C)	2710±300	0.034
FM73	5540±200	0.112

exceedingly short out-time at room temperature (<3 hr), while our adhesive resin produces consistent LSS after more than 12 months of room-temperature storage.

7. Conclusions

The results presented in this report include a number of preliminary studies, which have established the importance of a “materials-by-design” approach to developing new adhesives for use with unique processing technologies. This report demonstrates that a design approach to materials is a successful mechanism for developing adhesives with specific property targets. We successfully demonstrated the ability to sculpt and toughen e-beam adhesives, which are two-stage-cured epoxy/methacrylate seq-IPNs. Future work will involve evaluating the impact of alternate toughening materials (CTBNs, core-shell particles, thermoplastic particles, chain extenders, etc.) on the toughness and preparing alternate adhesive forms such as one-part and film adhesives with comparable performances.

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Appendix:
Synthesis of Methacrylate Network Coupling Materials

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Seq-IPN coupling agents connect the methacrylate and epoxy networks through chemical bonds, but these materials are not commercially available as methacrylates. As a result, partially methacrylated epoxide monomers were synthesized from various commercial diepoxides. The synthetic method for generating methacrylates from epoxides was patented by Doyle and Kennan.¹ The patent demonstrates complete conversion of epoxides to acrylates. It was necessary to modify the disclosed synthesis in order to improve product stability for partially converted monomers. In many instances, the final product did not possess long-term stability. Stable shelf-life resin was achieved for all resins by using a catalyst composed of a suitably chosen ratio of triphenyl stibine to triphenyl phosphine. The synthesized resins are designated by ARL #(*), where # designates the base resin for the synthesis and (*) designates the extent conversion of epoxide to methacrylate. The product from each synthesis is a mixture of mono-epoxy-mono-methacrylate (MEMM), diepoxyide (DE), and dimethacrylate (DM) for all difunctional epoxide starting materials. The MEMM is the coupling agent that was desired. Examples of synthesized MEMM materials are shown in Table A-1. The mole ratio of these materials was determined using HPLC where the column phase is 8/1/1 H₂O/acetonitrile/tetrahydrofuran, and the carrier phase is methanol (CH₃OH). The HPLC spectrum of a 50% methacrylated EPON 828 epoxide resin, ARL1(50), is shown vs. pure EPON 828 in Figure A-1. Figure A-2 shows the HPLC characterization spectra for a partially (50%) methacrylated resin prepared from EPON 834, a chain-extending bis-phenol A formulation, while Figure A-3 shows completely methacrylated EPON SU-8, an octafunctional epoxide. The reference peak in all three figures is the conversion of the DGEBA (n=1) at 9.4 min. Table A-1 shows the conversion stoichiometry for all of the resins evaluated under this project. The monomer compositions are determined by the ratio of individual peak intensity to the sum of peak intensities from 8 to 12-min elution time. The monomer concentrations are recorded for each monomer in the resin and are listed by mole ratio in Table A-1. The mole ratio of these components can be controlled by changing the ratio of initial acid to epoxide. Quantitative determination of the remaining epoxide content is used to maintain epoxy-amine stoichiometry.

¹ Doyle, T. E., F. Fekete, P. J. Kennan, and W. J. Plant. "Combination Catalyst-Inhibitor for Beta-Hydroxy Carboxylic Esters." U.S. Patent 3,317,465, 1967.

Table A-1. Names and Conversion Specifications for U.S. Army Research Laboratory (ARL)-Synthesized Monomers

Designated Name	Moles Acid per Mole DE	Initial DE	Mole Ratio of Monomers (MEMM:DE:DM)
ARL-1(50)	1	EPON 828	0.5:0.25:0.25
ARL-1(66)	1.3	EPON 828	0.1:0.42:0.48
ARL-2(50)	1	EPON 834	0.51:0.24:0.25
ARL-2(100)	2	EPON 834	0.08:0.0:0.92
ARL-3(100)	2	EPON SU-8	0.06:0.0:0.94
ARL-4(100)	2	EPON 1001F	0.08:0.0:0.92

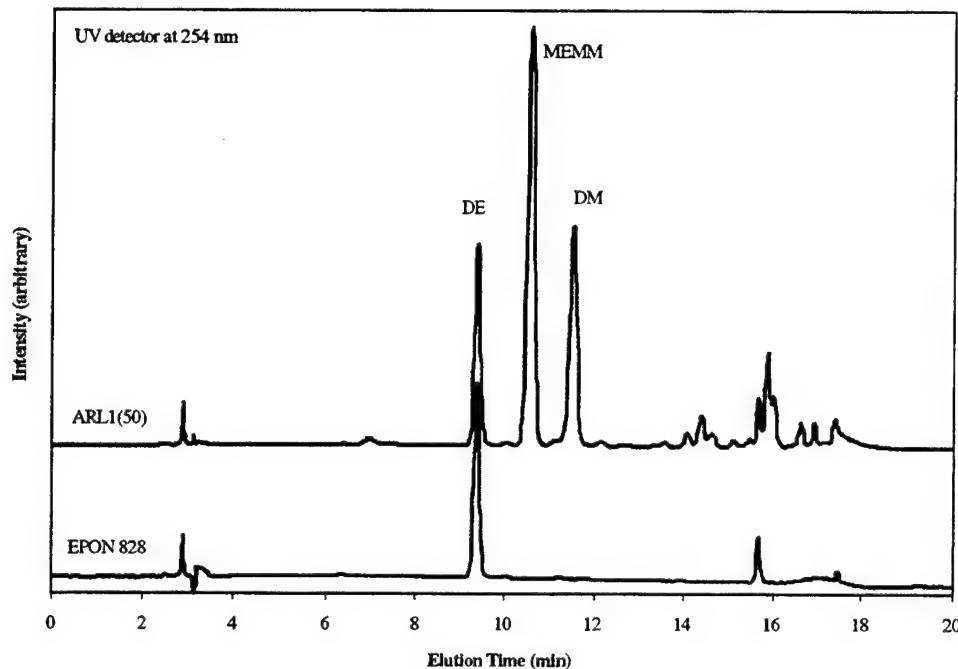


Figure A-1. HPLC Spectrum for ARL1(50) (Lot No. JMS011599) and EPON 828 Precursor. The Peak Areas for DE, MEMM, and DM Are Indicative of the Extent of Reaction and the Molar Composition of the Monomer Mixture. The Selected Spectrum Shows a Molar Distribution of Monomers 0.52:0.23:0.25 for MEMM:DE:DM.

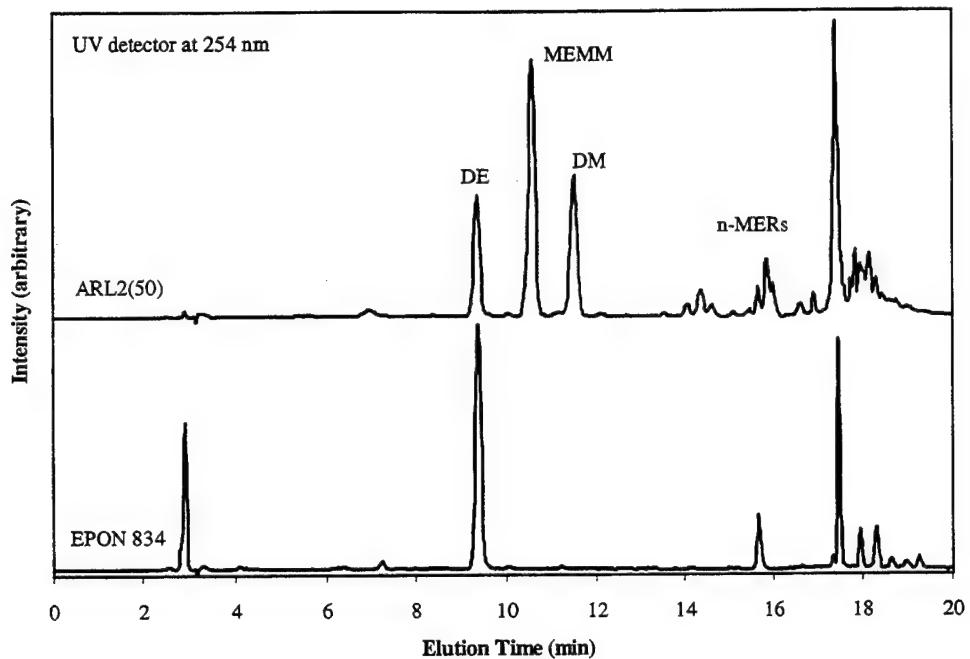


Figure A-2. EPON 834 HPLC Trace and After 50% Conversion of Epoxides to Methacrylate (ARL2[50]). Conversion Is Representative of All Experimental Studies.

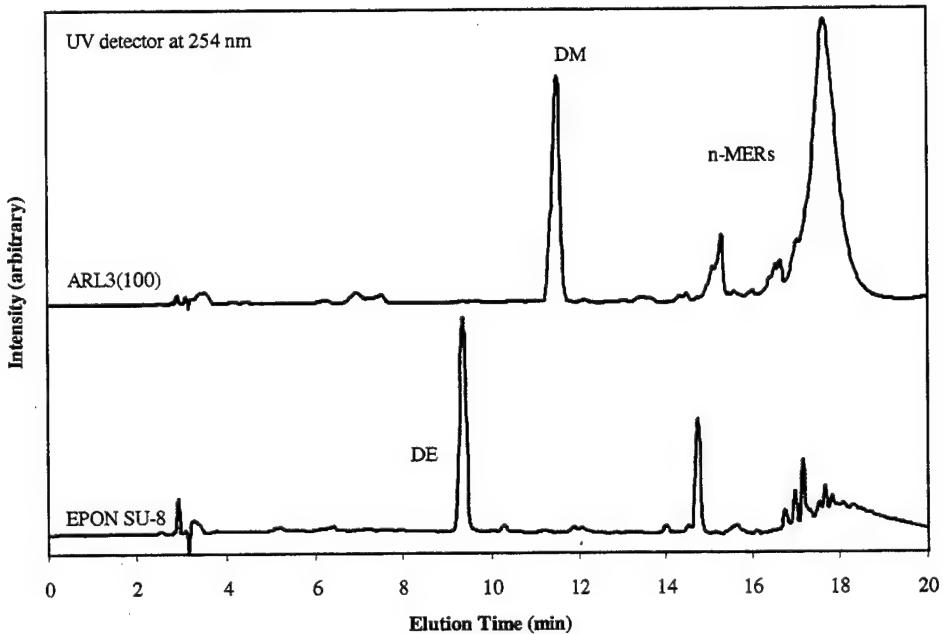


Figure A-3. SU-8 HPLC Trace and After 100% Conversion of Epoxides to Methacrylate (ARL3[100]).

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: AMSRL-WM-MB Aberdeen Proving Ground, MD 21005-5069			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-2270	
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